

Tannery Wastewater Evaluation and Remediation: Adsorption of Trivalent Chromium Using Commercial and Regenerated Adsorbents

AU Itodo^{1*}
ME Khan¹
DP Feka²
B Ogoh¹

¹Department of Chemistry, Federal University of Agriculture Makurdi, Nigeria

²Nigerian Institute of Leather and Science Technology, Samaru, Zaria, Nigeria

Abstract

The objective of this research is focus on pollutants evaluation and remediation of Tannery effluent discharged from Nigerian Institute of Leather and Science Technology (NILEST) Zaria, Nigeria using activated Carbons as adsorbents. The received, spent and Reborn Adsorbents (RGAC) were characterized using both classical (bulk density, ash content and iodine number) and instrumental (AAS, SEM, FTIR and UV-Vis Spectrophotometer) techniques. The role of different operating parameters on Cr uptake was investigated from a batch adsorption mode. Data generated were fitted into four isotherm models viz; Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The earlier estimated chromium level in the tannery effluent which was above WHO and NESREA permissible limits was considerably reduced via adsorption. On the general, results show good significance in the adsorption behavior of the regenerated adsorbent compared to the commercial sample.

Keywords

Wastewater; Pollutants; Remediation; Adsorption; Tannery Effluent; Isotherms; NILEST

Introduction

Industries have been fingered as the major institutions since the last four decades, responsible for diverse environmental and human catastrophes; hence they are a major contributor to environmental degradation and pollution. Environmental pollution due to appreciating industrial activities is unquestionably some of the most important problems of this century (Ladwani et al., 2012).

Tannery wastewater is highly polluted in terms of the content of its Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Suspended Solids (SS), nitrogen, conductivity, sulphate, sulphide and chromium (Mondal et al., 2005) and in most developing countries tannery effluents are discharged directly into sewers or water bodies without treatment [1,2]. High BOD content of an effluent affects the survival of gill breathing animals of the receiving water body and high COD value indicate toxic State of the wastewater, including the presence of biologically resistant organic substances. High level of ammonia (NH₃) is toxic to aquatic organisms and excess nitrogen will cause eutrophic condition. The high salinity and Total Dissolved Solids of effluents may result in physiologically stressful conditions affecting some species of aquatic organisms due to alterations in osmotic conditions. Changes in the ionic composition of water can also eliminate some species while promoting population growth of others [3]. Chrome Tan liquor is greenish in color and highly toxic and acidic with pH 3.1 to 6.0. The waste contains a high concentration of trivalent chromium ranging from 100 to 5500 mg/L. Hexavalent chromium is not generally present in the waste chrome liquor because of the reducing agent used and one bath process utilized [4].

The manufacture of leather has evolved into a significant source of livelihood in many industrialized and developing countries, [5] reported an estimated production capacity of 1.8 billion metric tons of leather yearly, with a larger part of the product processed in Africa and Asia, factored by the high labour intensity involved the manufacture of leather. Procedures employed by most developing countries in leather tanning is still at the traditional level and are not technologically compactable or designed for use with chemical and water. As estimated, the total wastewater discharge from tanneries runs to about 400 million m³ each year. The industry has been painted negatively in the society owing to its high pollutant composition, health and environmental implication is a negative to the sitting of the leather industry. The difficulty in treating tannery effluent owes it to the complex nature of the wastewater produced, leading to various environmental regulations and laws in many developing countries being passed especially in the last ten years.

Adsorption is a phenomenon that occurs on the surface or pores of a solid (sorbent),

Article Information

DOI: 10.31021/jwt.20181105
Article Type: Short Communication
Journal Type: Open Access
Volume: 1 **Issue:** 1
Manuscript ID: JWT-1-105
Publisher: Boffin Access Limited

Received Date: November 01, 2017
Accepted Date: December 15, 2017
Published Date: January 30, 2018

*Corresponding author:

AU Itodo
Department of Chemistry
Federal University of Agriculture Makurdi
Nigeria
Tel. No: +2348039503463
E-mail: itodoson2002@gmail.com

Citation: AU Itodo, ME Khan, DP Feka, B Ogoh. Tannery Wastewater Evaluation and Remediation: Adsorption of Trivalent Chromium Using Commercial and Regenerated Adsorbents. J Water Technol Treat Methods. 2018 Jan;1(1):104

Copyright: © 2018 Itodo AU, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution 4.0 international License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

it is characterized by the available surface area and is a function of the partial pressure (or concentration in aqueous solutions) of a chemical species (solute) [6]. Adsorption occurs if the attractive force between the solute and Adsorbent is greater than the cohesive energy of the substance itself. Adsorption isotherms are important for the description of how adsorbates will interact with an Adsorbent and are critical in optimizing their use [7]. Correlation of equilibrium data using a theoretical or empirical equation is useful for adsorption data interpretation and prediction. Several mathematical models are applicable in describing experimental data of adsorption isotherms.

Langmuir adsorption isotherm, originally developed to describe gas-solid-phase adsorption onto activated carbon, has traditionally been used to quantify and contrast the performance of different bio-sorbents. In its formulation, this empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent. In its derivation, Langmuir isotherm refers to homogeneous adsorption and can be represented as Equation. 1

$$q = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

Where K_L (L/mg) and q_m are Langmuir isotherm constants [8].

Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. This model has been expressed either as a non-linear (Eq. 2) or linear (Eqn. 3) form of the model:

$$q_e = K_F C_e^{\frac{1}{n_F}} \quad (2)$$

$$\log q_e = K_F + \frac{1}{n_F} \log C_e \quad (3)$$

K_F and n_F are Freundlich constants obtained from the intercept and slope of the linear plot of $\log q_e$ vs $\log C_e$. They are empirical constants which are indicators of sorption capacity and adsorption intensity, respectively [8,9].

The Temkin isotherm assumes that the heat of adsorption of all the molecules increases linearly with coverage. The linear form of this isotherm can be given by:

$$q_e = \frac{RT}{b_T} \ln a_T + \frac{RT}{b_T} \ln C_e \quad (4)$$

R is universal gas constant (8.314 J/molK), T is absolute temperature (K) and b_T is Temkin isotherm constant. The slopes and intercept are obtained from the graphical plot against \ln [10,11].

The linear form of the Dubinin- Radushkevich isotherm can be expressed as:

$$\ln q_e = \ln q_D - B \epsilon^2 \quad (5)$$

Where q is the theoretical saturation capacity (mg g^{-1}), B is a constant related to mean free energy of adsorption per mole of the adsorbate (mol^2/J) and ϵ is the polanyi potential which is related to equilibrium is given by:

$$\epsilon = RT \ln(1 + C_e) \quad (6)$$

Where, R is the Universal gas constant (8.314 J/mol/K) and T is the temperature in Kelvin. E the mean sorption energy is calculated using the following relation in Equation. 7:

$$E = \frac{1}{(2B)^2} \quad (7)$$

Based on this energy of activation one can predict whether an adsorption is physisorption or chemisorptions. It is general applied to express the adsorption process occurring onto both homogeneous and heterogeneous surfaces, the plot of $\ln(q_e)$ vs ϵ^2 is used to test the suitability of the data to this model [12].

BET isotherm is a theoretical equation, most widely applied in the gas-solid equilibrium systems. This is a more general, multi-layer model. It assumes that a Langmuir isotherm applies to each layer and that no transmigration occurs between layers. It also assumes that there is equal energy of adsorption for each layer except for the first layer. Its extinction model related to liquid-solid interface is exhibited as Equation. 8:

$$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)\left(\frac{C_e}{C_s}\right)]} \quad (8)$$

Where C_{BET} , C_s , q_s , and q_e are the BET adsorption isotherm (mg/L), adsorbate monolayer saturation concentration (mg/L), the theoretical isotherm saturation capacity (mg/g) and equilibrium adsorption capacity (mg/g), respectively. As C_{BET} and $C_{BET}(C_e/C_s)$ are much greater than 1, the equation is simplified as Equation. 9 [13,14].

$$q_e = \frac{q_s}{1 - \left(\frac{C_e}{C_s}\right)} \quad (9)$$

Among several Authors, [15] worked on Removal of Chromium from Tannery Effluent Using Bio-adsorbents. On a similar quest, [16] investigated the adsorptive removal of chromium ions from tan liquor using. The Neem Sawdust (NS) gave removal efficiency of 84% at contact time of 120 minute [16]. We now consider a reclamation approach by regenerating spent commercially available activated carbon for a possible reuse in Cr uptake from the Nigerian Institute of Leather and Science Technology (NILEST) Zaria, Nigeria. This present work also investigated pollution load of chrome tan- wastewater and arrayed five isotherm models for interpretation of the sorption phenomenon [17].

Materials and Methods

Reagents used were of analytical grade and prepared in line with standard methods as described in the Manual for Standard Analytical Procedures (1999) except otherwise Stated. The FTIR spectrum was recorded on a Fourier Transform Infrared Spectrometer (Agilent technologies Cary 630), scanning electron microscope (SEM) images of virgin, effluent loaded and Chemically regenerated activated carbon at selected magnifications was observed using SEM (Phenomenon Pxi, MVE016477830). UV-Visible (Agilent 8453E) Spectrophotometer was used to study the absorbance of both treated and untreated effluent. The procedure was carried out at a pre-determined wavelength (λ_{max}) of 353nm. Atomic adsorption Spectrophotometer (Varian AA240FS) was used to estimate the concentrations of Cr present.

Study Area

The study area, Nigerian Institute of Leather and Science Technology (NILEST) is an Institution of higher learning located in Samaru-Zaria. Coordinates are, Latitude 11.1667°, Longitude 7.6333°. It is situated in an area dominated by Schools and research Institutes, Majority of the dwellers are civil servants and farmers

Sampling

Sampling was carried out in accordance with methods described by Kawser et al. as shown in (figure 1) [18]. Effluent samples by lowering a pre-cleaned 4L glass bottle (previously washed with 0.1M HNO_3 before rinsed with distilled water) into different depths of the effluent, allowed to overflow, withdrawn, sealed and stored at 4°C till required for further analysis. Temperature, total dissolved solids, pH and conductivity were determined *in situ*. Effluent sample to be used for Cr analysis was treated with concentrated HNO_3 in order to lower the pH of the sample to less than 2 before refrigeration. Method and duration of the preservation adopted was described by APHA

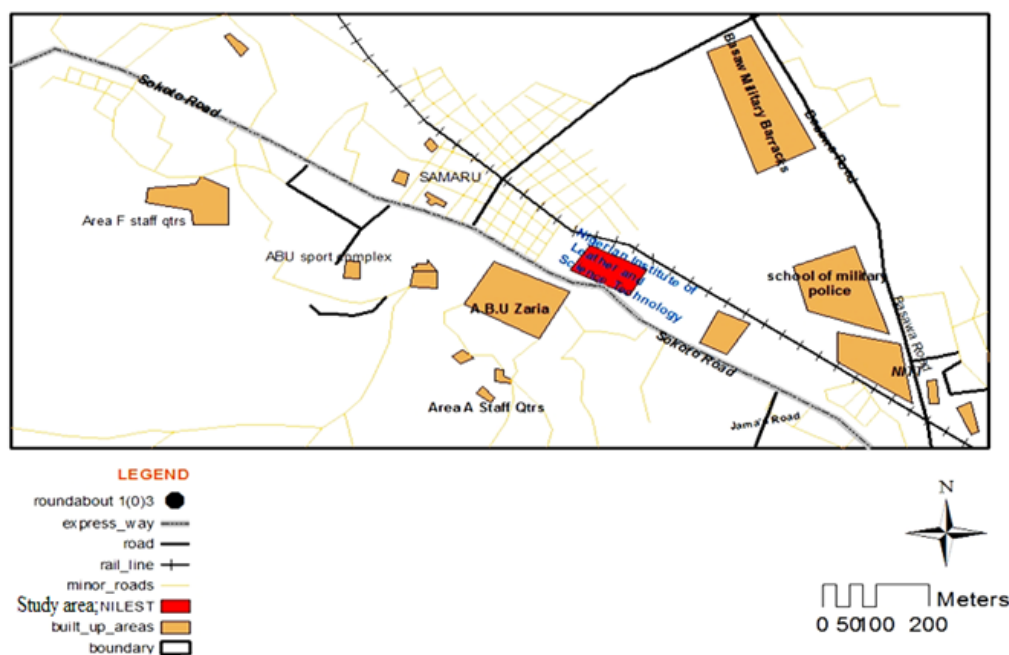


Figure 1: Map showing Study Area and Sampling Site in Red

Freeman et al., (2009) and Roger (2002) [19].

Characterization of tannery effluent

The sampled effluent was analyzed for their physicochemical parameters as well as active functional groups and UV-profile following procedures outlined in the standard method for the examination of water and wastewater [19,20,21]. These parameters include Temperature, Electrical conductivity, Total Dissolved Solids, pH, Turbidity, Biochemical Oxygen Demand, (BOD), Chemical Oxygen Demand (COD), Chlorides and Sulphides. Two techniques viz; classical (bulk density, ash content and iodine number) and instrumental (AAS, SEM, FTIR and Uv-vis Spectrophotometer) were used. Results were reported as mean values of triplicate analysis.

Batch Adsorption Experiments

Batch experiments were conducted at room temperature ($25 \pm 2^\circ\text{C}$) following the approach reported [22] with a slight modification. 200 mL of adsorbate solution of different concentrations was collected in the 250 mL conical flask, and 1g of each adsorbent was separately added and maintained at the optimized pH 6 and contact time for equilibration. The solution was stirred in mechanical shaker at 120 rpm at room temperature. After that the solution was filtered and the concentration of the filtered solution was determined by Atomic Absorption Spectrophotometer (Varian AA240FS). The effect of various parameters on the rate of adsorption process was observed by varying contact time, Adsorbent concentration, temperature, and pH of the solution. The solution volume was kept constant.

Chemical regeneration of activated carbon

Regeneration of exhausted activated carbon was carried out in the laboratory using method adopted from Abbas and Waleed, (2008). The exhausted activated carbon (50 g) was weighed by electric balance (Mettler AE200) and mixed with 600 mL 20% ethanol in a 1 L pyrex beaker. The mixture was agitated using a magnetic stirrer (IKA Hitachi RT5) at 200 rpm for 4 h at $25 \pm 2^\circ\text{C}$. The washing liquid was replaced three times during this process, then with 0.1 M NaOH and rinsed with distilled water. The pH of the activated carbon solution was adjusted to pH 7 using 0.1 M HCl. Washed adsorbent was dried in the oven (Gallenkamp BS 0V-160) at 200°C for 3 h and stored as Regenerated Granular Activated Carbon (RGAC).

A batch adsorption experiment similar to the one earlier

described was carried out using the regenerated granular activated carbon. The efficiency of the regenerant is judged on the adsorption quantity of activated carbon using equation 10:

$$\text{Regeneration Efficiency (RE\%)} = \frac{q_r}{q_0} \times 100\% \quad (10)$$

Where q_0 and q_r are quantity of Cr (adsorbate) adsorbed per unit weight of commercial activated carbon and quantity of Cr adsorbed per unit weight of regenerated activated carbon, respectively (Martine and Ng, 1984).

Discussion

SEM Characterization

Surface morphology of adsorbents was studied by scanning electron microscopy (Plate 1).

Plate 1 SEM micrograph of virgin GCAC (Top left), spent GCAC (Top right), RGAC (bottom left) and spent RGAC (Bottom right)

Physical Inspection

Physical examination of untreated effluent sample revealed high pollution density as evident by brown colouration, foul odour, microbial activities etc. Similar result was reported [23].

Characteristics parameters of adsorbents

Table 1 compares the physicochemical properties of received and derived adsorbents. Properties fell within range with reported slight differences resulting from losses linked to chemical treatment (bulk density and ash contents) and the measure of micro-porosity (iodine adsorption number).

Iodine adsorption number (an affinity of adsorbent for micro size pollutant) measures activity level and its values are reported in mg/g (typical ranges are from 500-1200). From result displayed on Table 1, High IAN values of 353.12 ± 0.02 (mg/g) for GCAC and 218.01 ± 0.02 for RGAC, indicates the suitability of the adsorbents under consideration in the removal of micro (small) size contaminants. It is a measure of micro-pores and it is used as an indication of the total surface area. Sorbents with high iodine number performs better in removing small sized contaminants [24]. It is the most fundamental parameter used to characterize the performance of activated carbon.

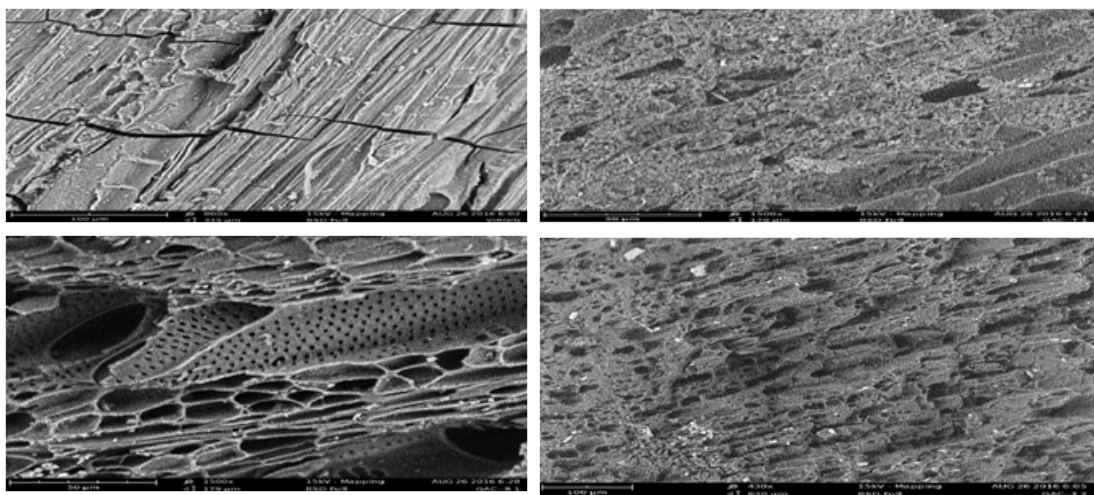


Plate 1

Parameter	Adsorbents	
	GCAC	RGAC
Bulk Density (g/cm ³)	0.10 ±0.02	0.08 ±0.02
Iodine Adsorption number (mg/g)	353.12 ±0.02	218.01 ±0.02
Ash Content (%)	1.00 ±0.02	2.40 ±0.02
Moisture Content (%)	1.02 ±0.02	1.10 ±0.02
Volatile matter (%)	12.00 ±0.02	18.21 ±0.02

Table 1: Physicochemical parameters of adsorbents

High value indicates high degree of activation as documented [24]. The bulk density value of the adsorbents are given in Table 1 above and are in agreement with the values reported in literatures [25,26]. Low ash content of an activated carbon makes it attractive for adsorption studies, high ash content means interference with pore structure development is likely to occur especially during regeneration and thus, adsorption will be less. Result is in agreement standard values for most commercial CAC [26]. This represents the bulk mineral matter after carbon, oxygen, sulphur and water has been driven off during combustion.

Volatile matter is an index of gaseous fuels present in the carbon. The volatile matter for the GCAC stands at 12 %, while that of RGAC is 18.21%; the higher value indicate removal of adsorbed volatile matter after using the GCAC for treatment of the effluent. This refers to components of coal other than moisture, which are liberated at high temperature in the absence of air.

Physicochemical properties of Tan Effluent (T_{eff})

Table 2 shows the physicochemical properties of untreated tan effluent (T_{eff}). Data compared to those of existing legislations [27,28] unveiled an indication of high pollution loading of effluent. Similar to this was the report of similar studies [18,29,30].

These higher values for COD and BOD suggest possibility of depletion of natural oxygen present in the effluent [31]. Evaluated pH value for T_{eff} fall within the WHO and NESREA acceptable limits for the discharge of wastewaters into both surface waters and sewers vary, these ranges are from pH 5.5 to pH 10.0. The present study gives the alkalinity value of the effluent at 225 mg/L CaCO₃. Alkalinity is a chemical measurement of a water’s ability to neutralize acids, this is a measure of the buffering capacity of water is ability to resist a change in pH when acids or bases are introduced into it [32]. The high acidity will contribute to corrosiveness and influence chemical reaction rates, chemical speciation and biological processes. Acidity of water is it’s quantitative to react with a strong base to a designated pH [33]. Estimated chloride concentration of 579.82 mg/L exceeds the discharge limit set [27,28] (250.00 mg/L). Chloride is introduced into

tannery effluents as sodium chloride usually on account of the large quantities of common salt used in hide and skin preservation or the pickling process [32]. Being highly soluble and stable, it is not affected by effluent treatment and nature, thus remaining as a burden on the environment. Sulphide concentration (450.00 mg/L) in the effluent of the present study is on a high side. Sulphide causes depletion of oxygen in water [33,34]. reported that the upper concentration limit of sulphide in water intended for human consumption is 250 mg/L. Nitrite (NO₂) concentration (0.450 mg/L) in this study, falls below the WHO (3.00 mg/L) and is at the recommended level for NESREA (0.5 mg/L)[28]. Cr concentration (148.92 mg/L) was determined and found to be highly above the WHO limit (2.00) and NESREA whose values ranges 1.50-2.00 mg/L [29,30,28].

Adsorption Studies

Table 4 presents results on removal or adsorption or efficiency (%RE). This study indicated the suitability of using both adsorbents for the removal of Cr in aqueous solution through batch adsorption studies. Mean value of less than 61% could be linked to an early report where high IAN values was reported to favour adsorption of micro rather than medium size pollutants [34].

Effect of pH

T_{eff} – GCAC showed highest % removal of Cr at pH 6 for GCAC and at pH 8 for RGAC. The results shown in

Figure 2 indicate that maximum uptake of Cr ions takes place at pH 4 and decrease in adsorption capacity on either side of pH 4. The removal of Cr is Ph dependent because the surface of activated carbons are negatively charged at certain pH [35], the decrease in adsorption capacity in the low pH region would be expected as the acidic medium would lead to an increase in hydrogen ion concentration which would then neutralize the negatively charged carbon surface thereby decreasing the adsorption of the positively charged cation.

Effect of adsorbent dose

The removal of Cr was found to be highest with an adsorbent dosage of 2.5g, achieving above 60 % Cr removal for GCAC and 55

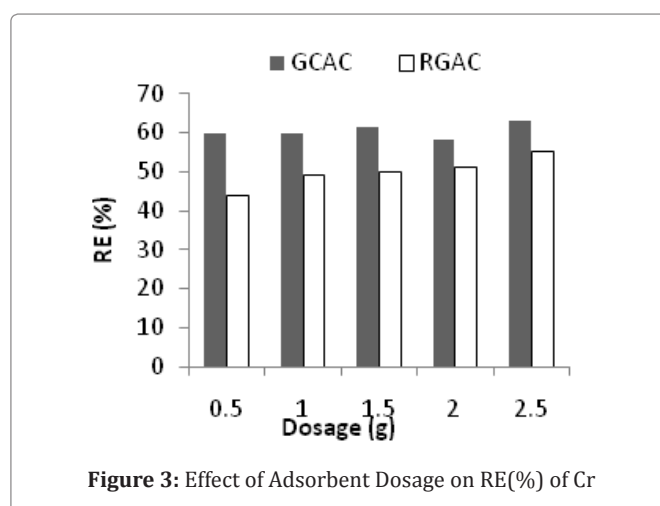
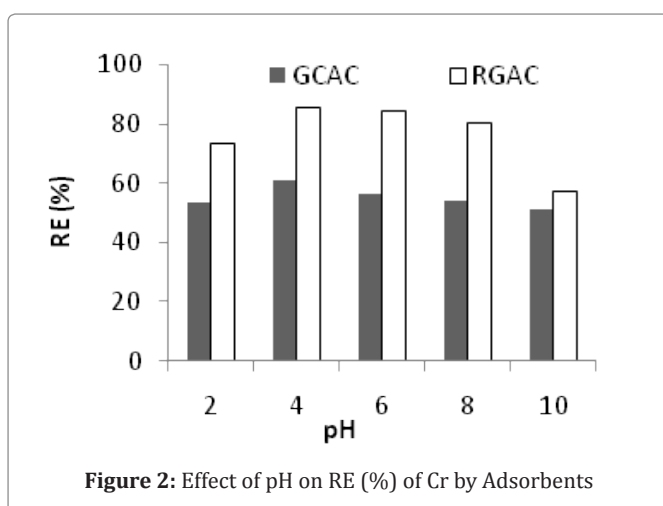
Parameters	Values		
	Current study	(WHO,2000)	(NESREA, 2009)
Initial Colour	Brown	Light permeable	-
Odour	Objectionable	-	Odourless
pH	8.6	6.5-9.5	6.0-9.0
Conductivity ($\mu\text{S}/\text{cm}$)	1348	1200	-
TDS (mg/L)	8111	2100	2000
BOD (mg/L)	942.0	30.0	30.0
COD (mg/L)	1239.0	250.0	60.0
Alkalinity(mg/L CaCO_3)	225	-	-
Acidity (mg/L CaCO_3)	15	-	-
Chloride (mg/L)	579.8202	250	250
Sulphide (mg/L)	450.00	1.0	0.20
Cr (mg/L)	148.917	2.0	1.5-2.0
Nitrite(mg/L)	0.450	3.0	0.5

Table 2: Physicochemical properties of T_{Eff} and Legislative discharge limit

Vib. Freq (cm^{-1})	Observed Frequencies (cm^{-1})			Functional group
	GCAC	SGCAC	RGAC	
1000-690	1032.5, 752.9	667.2	-	C-H
1160-1050	-	1636.3	1162.9	C-O stretch,
1285-1250	1271.0	-	-	C-O stretch; CH_3 symmetric deformation; N-O
1640-1550	1524.5	1636.3	1625.1	N-H bend; $\text{C}\equiv\text{C}$ stretch; $\text{C}=\text{C}$ stretch
2140-2080	2113.4	-	2083.6	$\text{N}=\text{N}=\text{N}$, Anti-symmetric stretch; $\text{C}\equiv\text{C}$
2410-2280	2344.5	-	-	-PH; $\text{C}\equiv\text{N}$
3300-3250	-	3272.6	3246.5	O-H broad; O-H stretch; -NH stretch; $\equiv\text{CH}$ -H stretch

Table 3: FTIR spectra characteristics of virgin GCAC, spent GCAC and RGAC

Experiment	Co (mg/L)	Ce(mg/L)	RE (%)
T_{Eff} -GCAC	148.917	64.467	56.7
T_{Eff} - RGAC	148.917	59.626	60.0

Table 4: Removal Efficiency (%) of Cr from Tan Effluent using GCAC and RGAC

% removal for RGAC Figure 3. The increase in removal of Cr with adsorbent dose can be attributed to the introduction of more binding sites for adsorption. Similar results have been reported [36,37,38].

Effect of initial concentration

The RE (%) of Cr in the sample is influenced by the initial concentration adsorbate. The highest percentage removal by GCAC was 67 % and 96 % with RGAC Figure 4. Thus, at higher initial concentration, the percentage removal decreases. This could be linked to competition for attachment sites.

Figure 5 represents the effect of contact time on Cr uptake. Adsorption increases with increase in contact time. Equilibration was achieved at 60 min, after which desorption sets in.

FTIR Study

Table 3 is a summary of spectral characteristic typical of Figures 6 and 7 for FTIR Spectra of unspent, spent and regenerated adsorbents. Distorted peaks of Figure 6a (3246.2 cm^{-1}) compared to Figure 6b, clearly shows surface interaction between the adsorbent and the adsorbate. An aromatic nitro group also appears at 12710.65 cm^{-1}

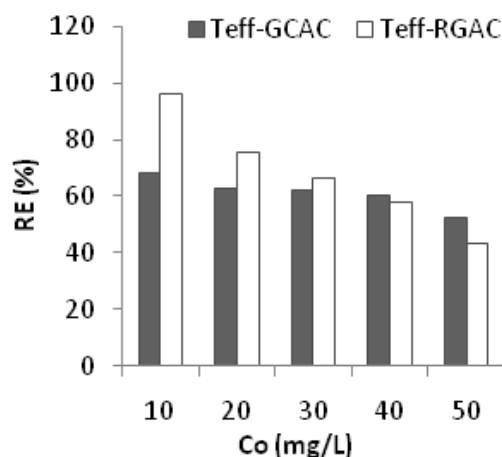


Figure 4: Effect of Concentration on RE (%) of Cr Activated Carbon

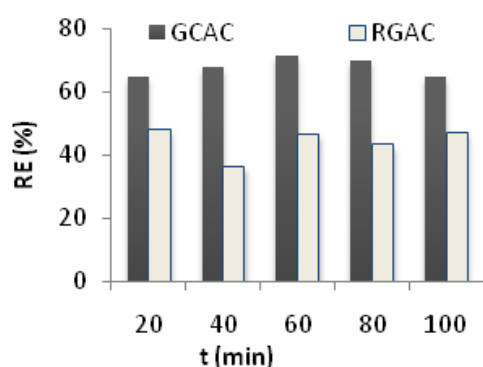
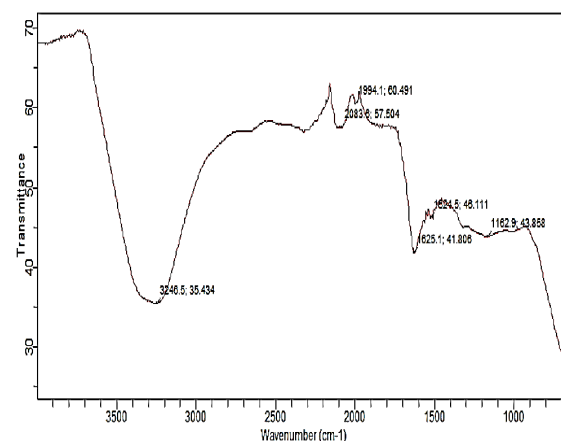
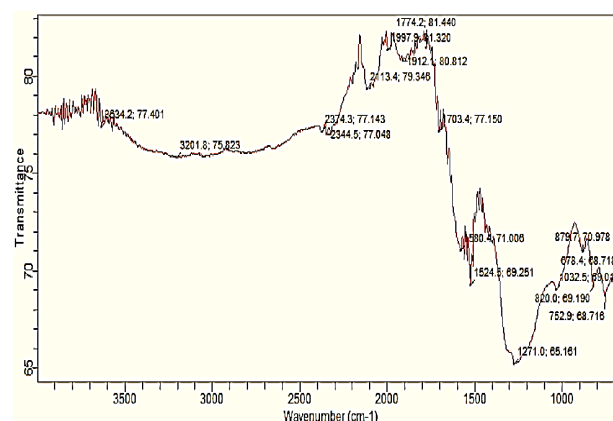


Figure 5: Effect of Contact Time on RE (%) of Cr



(a)



(b)

Figure 6: FTIR spectra of (a) GCAC (b) Teff loaded GAC

(C-H, C-N), 24113.4 cm^{-1} (C-H) and 1524.5 cm^{-1} (C=C) in Figure 6b are all functional groups attached to GCAC after adsorption. This is visible even in the shift of bands and is visible when compared to peaks shown in Figure 6a. Spectrum of T_{eff} - RGAC, displays strong bands adsorptions at 3280.1 cm^{-1} , for O-H, then 1626.1 cm^{-1} (C=C) to 1528.2 cm^{-1} (C=C-C), then at 10287.7 cm^{-1} to 1166.7 cm^{-1} (C-O) which appears distorted when compared to the RGAC and denotes adsorption.

SEM Characteristics of Adsorbents

Plate 1 is SEM micrographs of the GCAC at various treatment conditions. Plate 1 (bottom left) is the SEM image for RGAC revealing a more porous morphological structure over the GCAC. This could mean more site of adsorption or vacancies for pollutants occupation. The loaded SEM images show the adsorption of T_{eff} onto the adsorbents depicting the filled-surfaces of particles after adsorption, it is clearly seen that the caves, pores and surfaces of adsorbent were covered by adsorbed T_{eff} and consequently the surface has become smooth. It is notable that the T_{eff} adsorbed onto the adsorbent affected the surface structure.

Isotherm Studies

Table 5 represents the constants deduced from modeling generated equilibrium data four isotherm models namely; Langmuir, Freundlich, Temkin and the Dubinin-Radushkevich. Extent of model fitness was based on the coefficient of correlation (determination or applicability) values, R^2

Langmuir Isotherm R^2 value of 0.992 (GCAC) and 0.930 (RGAC) shows a good applicability of the model, indicating both monolayer

adsorption and heterogeneous surface conditions (Vinodhini and Das, 2010). In Langmuir theory, the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. The essential feature of the Langmuir isotherm is expressed by means of dimensionless constant separation factor (R_L). In this context, lower R_L , less than 1.0 reflects that adsorption is favourable. R_L value indicates the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Result from this work on favourable adsorption is in agreement [13].

Coefficient of regression recorded for the Temkin Isotherm was 0.993 and 0.879 for GCAC and RGAC respectively. It can be deduced that the isotherm model for GCAC has a better applicability than RGAC [39]. β_T is a constant related to the heat of adsorption, where a high value indicate strong interaction between Cr and the adsorbent. From the result, the constant β_T was 1.537 KJ/mol for GCAC and 0.137 KJ/mol for RGAC, indicating a weak interaction between Cr and the adsorbent. Temkin isotherm assumes that the heat of adsorption of the molecules increases linearly with coverage [10,40].

The Freundlich isotherm assumes a heterogeneous surface with non-uniform distribution of heat of adsorption over the surface. The R^2 values recorded for GCAC and RGAC are 0.938 and 0.958 respectively, indicating a slightly better applicability of this model to RGAC over GCAC, result recorded also gave the value of $1/n$ and K_F which represents Freundlich constants for adsorption intensity and capacity respectively. It is favourable for $1/n$ value to be less than 1 or an adsorption intensity (n) value greater than 1. $1/n$ indicate favourable uptake of adsorbate when $0.1 < 1/n < 1$. For this research, $1/n$ values for sorption of Cr on GCAC and RGAC gave values that are

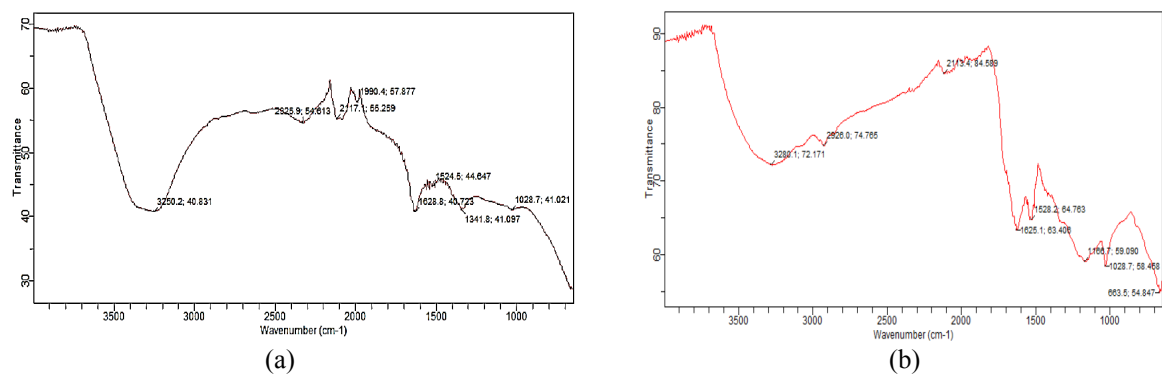


Figure 7: FTIR spectra of (a) RGCAC (b) TEff loaded RGAC

Isotherm Model	Constants	Values	
		T _{Eff} - GCAC	T _{Eff} - RGAC
Langmuir	R ²	0.992	0.93
	K _L	45.88	16.583
	q _m (mg/g)	3.63	15.258
	R _L	0.116	0.014
Freundlich	R ²	0.938	0.958
	1/n	1.754	1.081
	K _F (mg/g)	0.533	0.287
Temkin	R ²	0.993	0.879
	b _T (K J/mol)	1.537	0.137
	K _T	0.31	0.026
Dubinin-Radushkevich	R ²	0.933	0.998
	K _D (mol ² /KJ ²)	4 x 10 ⁻⁴	2 x 10 ⁻⁴
	q _s (mg g ⁻¹)	0.376	0.038

Table 5: Isotherm experimental constants for adsorption of Cr onto Activated carbon

above 1.0, with n values < 1.0, implying an unfavorable fitness of the model irrespective of the high R² values. The values are unlike those for good adsorption [41].

For Dubinin-Radushkevich isotherm model, R² value for GCAC and RGAC are 0.933 and 0.998, generally showing a good fit for this model but a better fit for RGAC. It is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [13]. This isotherm model is an empirical model initially conceived for the adsorption of subcritical vapors onto micropore solids following a pore filling mechanism.

Generally, all the models adopted for this study provide explanation on a particular sorption phenomenon. Considering the sorption of Cr on regenerated adsorbent RGAC, best fit coefficient of determination (R²) values follows the order; Dubinin-Radushkevich (0.998) > Freundlich (0.958) > Langmuir (0.930) > Temkin (0.879) isotherm models. The reverse trend was observed for the virgin GCAC.

Conclusion

Regeneration of Cr- loaded spent granular activated carbon and its adsorption studies was successfully carried out. Removal efficiencies were high for tannery wastewater detoxification and clarification. All the adopted and investigated isotherms gave explanation on certain adsorbent property. The best fit coefficient of regression (R²) value for the sorption of Cr on regenerated adsorbents follows the order of Dubinin-Radushkevich > Freundlich > Langmuir > Temkin. AAS analysis shows that the level of Cr in the tannery effluent is above WHO and NESREA permissible limits and could pose potential threat to the populace. However, results from this study unveiled a removal efficiency of up to 56 and 60 % using commercial and regenerated

activated carbons respectively. Results on the adsorption potentials of adsorbents from existing literatures and those of commercial adsorbent utilized in this study are in good agreement with those of our regenerated adsorbent. On the overall, GCAC and RGAC studied in this work established the potentials of chemically regenerated activated carbon for use in the treatment of pollutants (Cr) from tanneries.

References

- Verheijen L, Wiersema D, HulshoffPol L W, De Wit J. Livestock and the environment finding a balance: Management of waste from animal product processing. International agriculture centre Wageningen. The Netherlands. 1996
- Favazzi A. Study of the impact of the main policies and environment protection measures in Africa's leather industry. Principal: AssomacServiziSrl for UNIDO. 2002.
- Weber-Scannell PK, Duffy IK. Effects of total dissolved solids on aquatic organisms: A review of literature and recommendation for salmonid species. American Journal of Environmental Science. 2007;3(1):1-6
- Bosnic M, Buljan J, Daniels RP, Rajamani S. Pollutants in tannery effluent; International Scenario on Environmental Regulations and Compliance, UNIDO technical assistance project SF/EGY/97/167 managed by Ferenc Schmel, Industrial Development Officer, Vienna. 2003.
- Bosnic M, Buljan J, Daniels RP. Pollutants in Tannery Effluents; United Nations Industrial Development Organization (UNIDO), US/RAS/92/120 Regional Programme for Pollution Control in the Tanning Industry in South-East Asia. 2000

5. Chiou CT. Partition and Adsorption of Organic Contaminants in Environmental Systems. John Wiley and Sons, Inc. 2002
6. Wang S, Boyjoo Y, Choueib A. A comparative study of dye removal using fly ash treated by different methods. *Journal of Chemosphere*. 2005;60(10):1401-1407
7. Karadag D, Yunus K, Mustapha T, Ozturk M. A comparative study of linear and non-linear regression analysis for ammonium exchange by Clinoptilolite Zeolite. *Journal of Hazardous Materials*. 2007;(144):432-437
8. Singh, Gagneep K. Freundlich, Langmuir adsorption isotherms and kinetics for the removal of malachite green from aqueous solutions using agricultural waste rice straw. *International Journal Of Environmental Sciences*. 2013;4(3):250-258
9. Allen SJ, McKay G, Porter JF. Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *Journal of Colloid Interface Science*. 2004 Dec;280:322-333
10. Zohre S, Ataallah Soltani G, Mehdi A. Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes. *International Journal of Water Resources and Environmental Engineering*. 2010;2(2): 016-028
11. Itodo AU, Itodo HU. Application of Isotherm Studies on The Evaluation of Sorption Energies For Dyestuff Removal Onto Derived Thermo-Cracked Shea Nut Shells. *Electronic Journal of Environmental, Agricultural and Food Chemistry*. 2011 Jan;10(3):1979-1987
12. Hameed BH, Foo KY. Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*. 2010 Jan;156:2-10
13. Vergari Daniele. Sorption of Organic Pollutants by Carbon Nanoparticles. A Term Paper, Bodenmatte 14c-5647 Oberrüti: 02-718-187, 1st Term, Environmental Sciences. 2008 April;4
14. Xavier M, Logeswari A, Mano S. Removal of Chromium from Real Tannery Effluent by Using Bio-adsorbents. *International Journal of Engineering and Science*. 2013 March;2(7):35-40
15. Pushpendra K, Kanjan U. Adsorption of pollution load from tannery effluent by using Neem Sawdust as an adsorbent. *International Journal of Chemical Studies*. 2015;3(1):1-3
16. Ejikeme PM, Okoye AI, Onukwuli OD. Kinetics and isotherm studies of Cu^{2+} and Pb^{2+} ionx removal from simulated waste water by Gambeya seed shell activated carbon. *The African review of Physics*. 2011;6:0017
17. Islam BI, Musa AE, Ibrahim EH, Salma AA, Sharafa, et al. Evaluation and Characterization of Tannery Wastewater. *Journal Of Forest Products & Industries*. 2014;3(3):141-150
18. APHA. American Public Health Association, Standard Methods for the Examination of Water and Waste Water. 1999
19. AWWA. *American Water Works Association, WPCF -Workshop on Particle Correlations and Femtoscopy*, Standard Methods for the Examination of Water and wastewater; American Public Health Association, Washington-DC. 1995.
20. USEPA. United States Environmental Protection Agency, Engineered approaches to in situ bioremediation of chlorinated solvents; Fundamentals and Field applications, EPA-542-R-00-008, Cincinnati, OH. 2001.
21. Mulu Berhe Desta. Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (*Eragrostis tef*) Agricultural Waste. *Journal of Thermodynamics*. 2013
22. Krishnamoorthi S, Sivakumar V, Saravanan K, Sriram Prabhu TV. Treatment and Reuse of Tannery Waste Water by Embedded System. *Journal of Modern Applied Science*. 2009;3(1)
23. Itodo AU, Abdulrahman FW, Hassan LG, Maigandi SA, Itodo HU. Physicochemical parameters of Adsorbents from locally sorted H_3PO_4 and ZnCl_2 modified Agricultural wastes. *New York Science Journal*. 2010 Jan;3(5)
24. Erhan D, Kobyab M, Elif S, Ozkan T. Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. *Water SA*. 2004;30(4):533
25. Veena Devi B, Jahagirdar AA, Zulfiqar Ahmed MN. Adsorption of Chromium on Activated Carbon Prepared from Coconut Shell. *International Journal of Engineering Research and Applications (IJERA)*. 2012;2(5):364-370
26. WHO. World Health Organization Guidelines for Drinking Water Quality. First Addendum to the Third Edition Volume 1. Recommendations. 491-493.
27. NEREA. National Environmental Standards and Regulatory Equipment Agency, 6(96). The Federal Government Printer, Abuja, Nigeri. 2009.
28. Jahan MA, Akhtar N, Khan NMS, Roy CK, Islam et al. Characterization of tannery wastewater and its treatment by aquatic macrophytes and algae. *Bangladesh Journal of Scientific and Industrial Research*. 2014;49(4):233-242.
29. Salisu D, Mustapha H. Industrial pollution and implication on source of water supply in Kano, Nigeria. *International Journal of Engineering and Technology*. 2010 Feb;1
30. Hodgson IOA, Larmie SA. CSIR-WRIT Technical Report. Accra - Ghana.1998.
31. Snoeyink VL, Jenkins D. *Water Chemistry*; John Wiley and Sons, New York, 3rd Edition. 1980
32. Sawyer, Clair N, Carthy Mc, Parkin G. *Chemistry for Environmental Engineering*, 4th Edition. Tata McGraw-Hill Publishing Company Limited. 2000
33. Kobayashi A, Stenstrom M, Mah RA. Use of photosynthetic bacteria for hydrogen sulfide removal from anaerobic waste treatment effluent. *Water Research*. 1983;17(5):579-587. doi: doi.org/10.1016/0043-1354(83)90117-3
34. Suguna M, Siva Kumar MN, Venkata Subbaiah M, Krishnaiah A. Removal of divalent manganese from aqueous solution using Tamarindus indica Fruit Nut Shell. *Journal of Chemical and Pharmaceutical Research*. 2010 Jan;2(1):7-20
35. Namasivayam C, Yamuna RT. Utilizing biogas residual slurry for dye adsorption. *American Dyestuff Reporter*. 1994; 235-239
36. Sarioglu M, Atay UA. Removal of methylene blue by using biosolid. *Global NEST Journal*. 2006;(8)2:113-120
37. Verma VK, Mishra AK. Kinetic and Isotherm Modeling of Adsorption of Dyes Onto Rice Husk Carbon. *Global NEST Journal*. 2010;12(2):190-196
38. Chinenye AI, Okechukwu DO, Joseph TN. Adsorptive Removal of Vat Yellow 4 on Activated Mucuna Pruriens (Velvet Bean) Seed Shells Carbon. *Asian Journal of Chemical Sciences* 2016; 1(1)
39. Srivastava VC, Mall ID, Mishra IM. Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto Bagasse Fly Ash (BFA) and Rice Husk Ash (RHA). *Chemical Engineering Journal*. 2007 Aug;132(1-3):267-278. doi: doi.org/10.1016/j.cej.2007.01.007
40. Krishnamoorthy Anbalagan, Joseph C Juliet. Adsorption of chromium (vi) ion onto activated amla dust: Adsorption isotherms and kinetics. *Indian Journal of Chemistry*. 2004;43A:45-50